

US EPA ARCHIVE DOCUMENT

Consideration of Characteristics Influencing the Emulsification Factors for Vegetable Oil Spills

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Applicability of Emulsification Factors

- 40 CFR 112 Appendix E – Responses Resources for FRPs
 - Table 7 – **Emulsification Factors** for AFVOs
- Used to calculate planning volumes for Worst Case Discharges (WCDs) – Appendix D
 - Accounts for increase in volume that results when discharged oil forms emulsions
- On-water recovery volume
 - $\text{WCD} \times (\% \text{ Recovered Floating Oil}) \times (\text{Emulsification Factor})$
- Shoreline cleanup volume
 - $\text{WCD} \times (\% \text{ Recovered Oil from Onshore}) \times (\text{Emulsification Factor})$

Oils

Non Petroleum Oils

Petroleum Oils

Other

Vegetable Oils

Non Vegetable Oils

Citrus Oils, Fish Oils, etc

Animal Fats

Crude Vegetable Oils



Partially-refined Oils



Fully-refined Vegetable Oils

Emulsifiers

Non Edible Oils

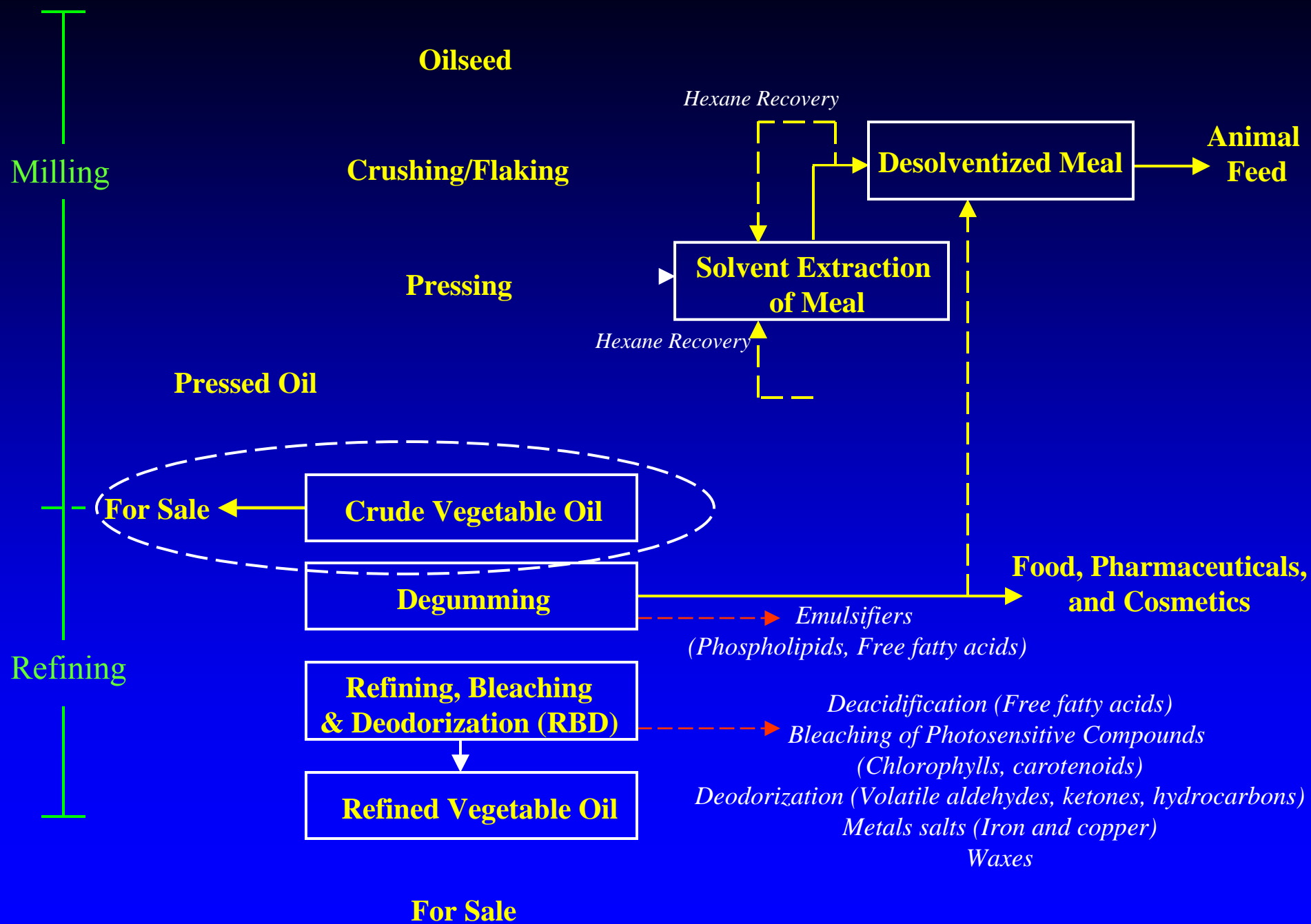
Edible Oils

Soap

Paints
Textiles
Fuels

Pharmaceuticals
Lubricants

Food



Why study crude vegetable oils?

- Oilseed milling facilities produce crude vegetable oils
- Milling processes are often separate from refining processes
- Thus, crude vegetable oils may be transported to refining facilities
- Crude vegetable oils are often transported in bulk through waterways

Crude vegetable oil composition

- Triglycerides
- Free fatty acids (*organic acids*)
- Metal salts
 - Iron, copper
- Photosensitive compounds
 - Chlorophylls, carotenoids
- Phospholipids
 - Phosphatides (*inositol, serine, ethanolamine, choline*)
- Tocopherols (*Vitamin E*)
- Plant sterols (*phytosterols*)
- Sulfur

In the presence of oxygen, these compounds reduce the oxidative stability of unsaturated oils via autocatalytic and photocatalytic reactions

Partially-refined vegetable oils

- Usually degummed with some RBD
- May need further processing before use

Fully-refined vegetable oils

- RBD-processed oils

- Triacylglycerols (TAGs)
- ~ 95% composition of crude vegetable oil
- Glycerol esters of fatty acids
- Fatty acid composition makes the type of vegetable oil unique
- Fatty acid composition can vary with cultivar

Compounds in crude vegetable oils that have amphiphilic properties

- Phospholipids
 - Phosphatidyl Choline
 - Phosphatidyl Inositol
 - Phosphatidyl Ethanolamine
 - Phosphatidyl Serine
 - Phosphatidic Acid
- Glycerophospholipids
- Free Fatty Acids
- Monoacylglycerols (MAGs) and Diacylglycerols (DAGs)

Experimental Setup

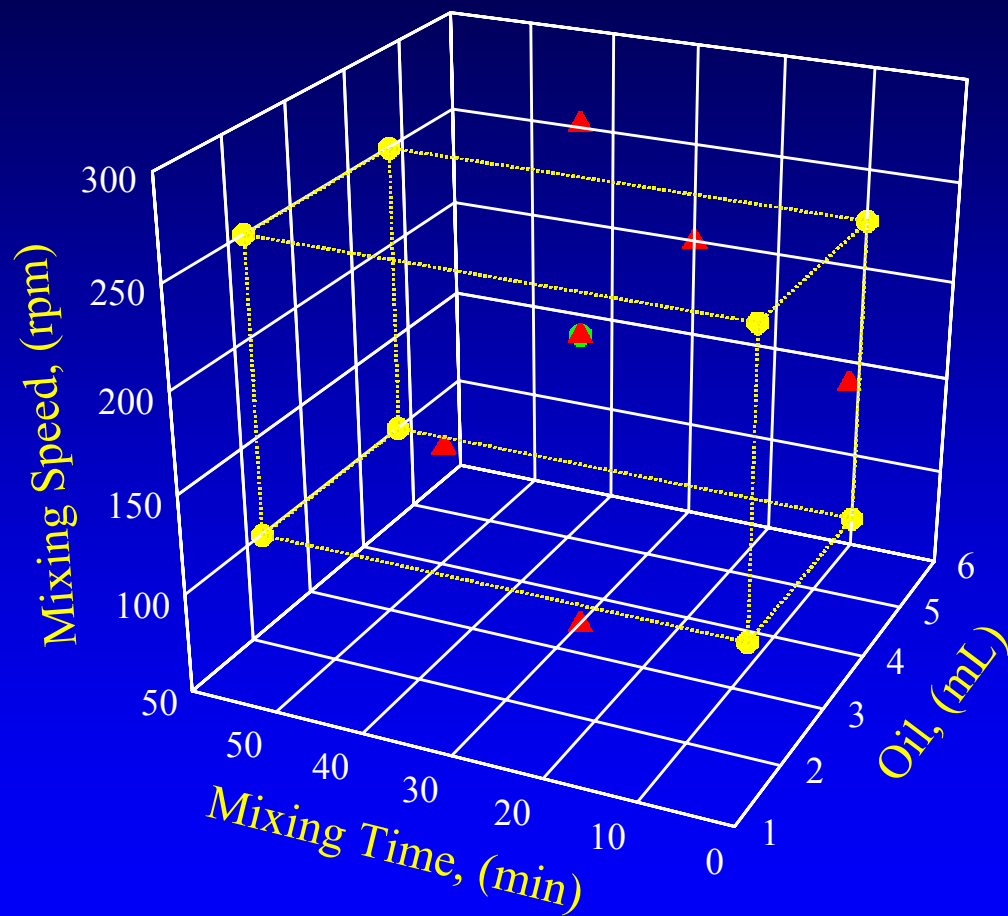
“modified” Central Composite Design

- Widely used technique in exploratory experiments
- Central Composite Designs (CCD) are good screening tools
- Multiple independent factors can be evaluated from few sampling events
- Data can be fitted to a response surface model to identify key factors
- Eliminating unresponsive factors allows researchers to refocus limited resources
- This experimental setup used a “modified” CCD design: “star” elements are offset

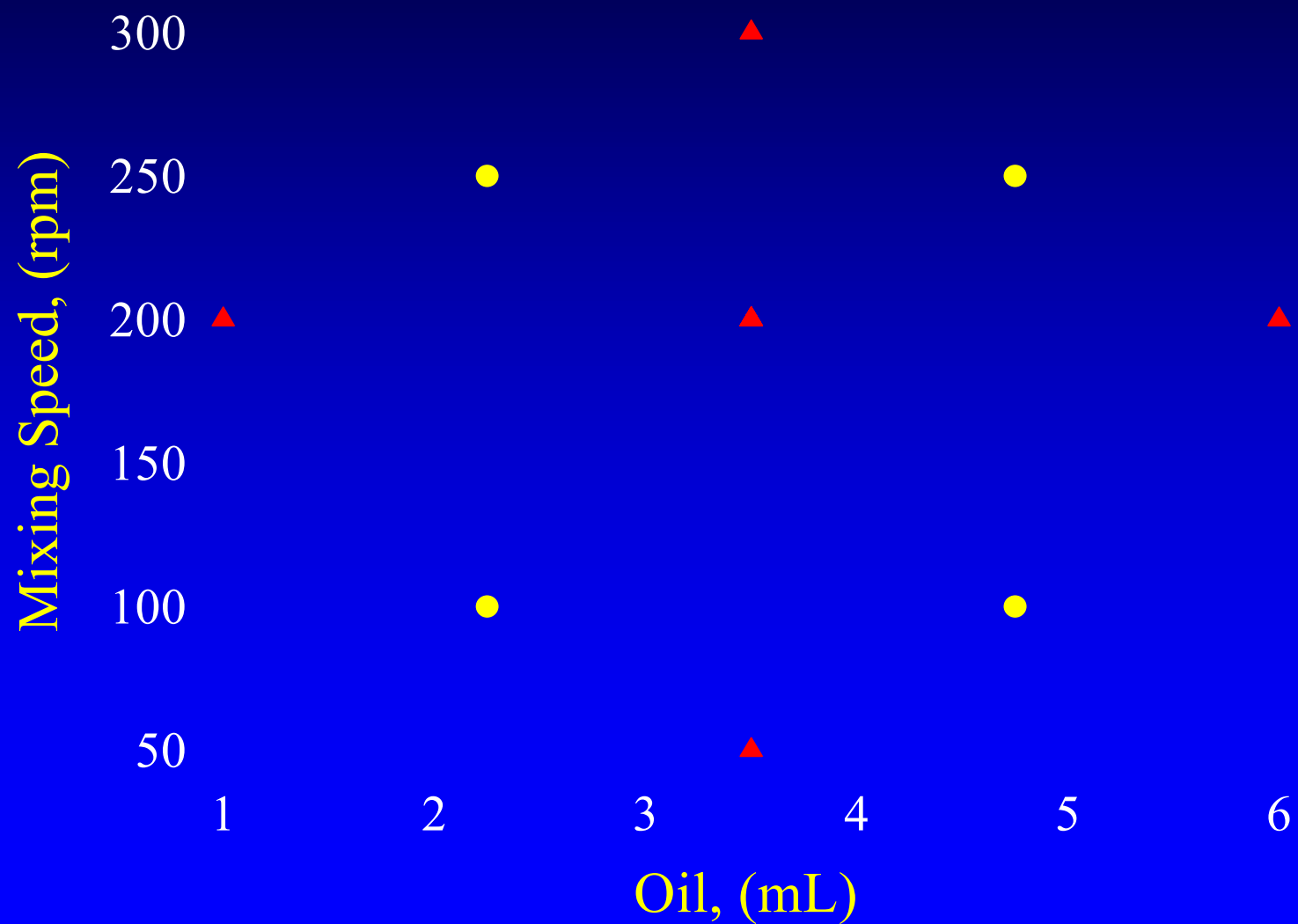
Experimental Setup: Factors Considered

- Five factors considered
 - Mixing time (1, 5, 30, 60, 180 minutes)
 - Mixing speed (50, 100, 200, 250, 300 rpm)
 - Oil:water ratio (1.00, 2.25, 3.50, 4.75, 6.00 mL oil) : (30 mL water)
 - Salinity (0, 16, 32 g/L NaCl)
 - Temperature (10°C and 25°C)
- Main elements = 2^k
- Since temperature is considered separately, $k = 4$
- 8 elements apiece at 0 and 32 g/L salinity satisfy the 2^k requirement
- “Star” elements = $2k - 1$ (or 7), satisfied at 16 g/L salinity
- Two “center” points for 0 and 32 g/L salinities
- Total of 25 samples (or elements) for each experimental run

Experimental Design: mCCD

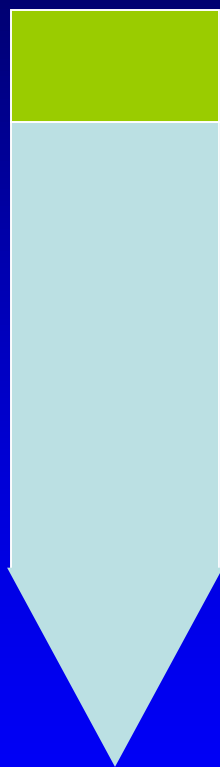


Experimental Design: mCCD - Plane View



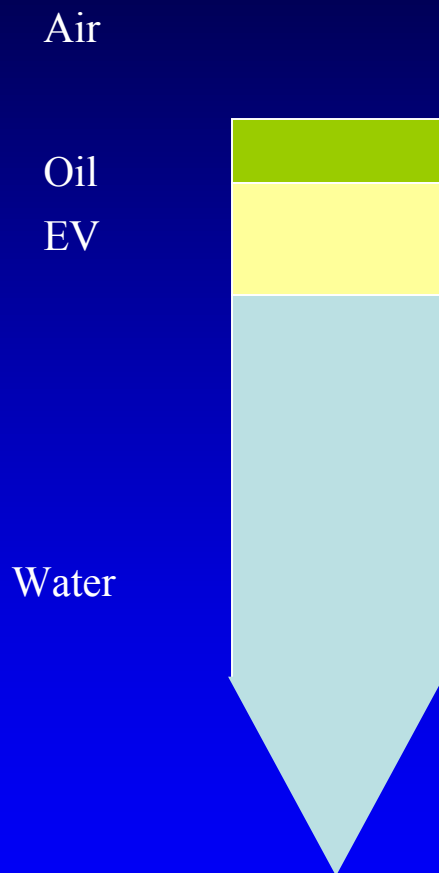
Initial Conditions

Air
Oil
Water



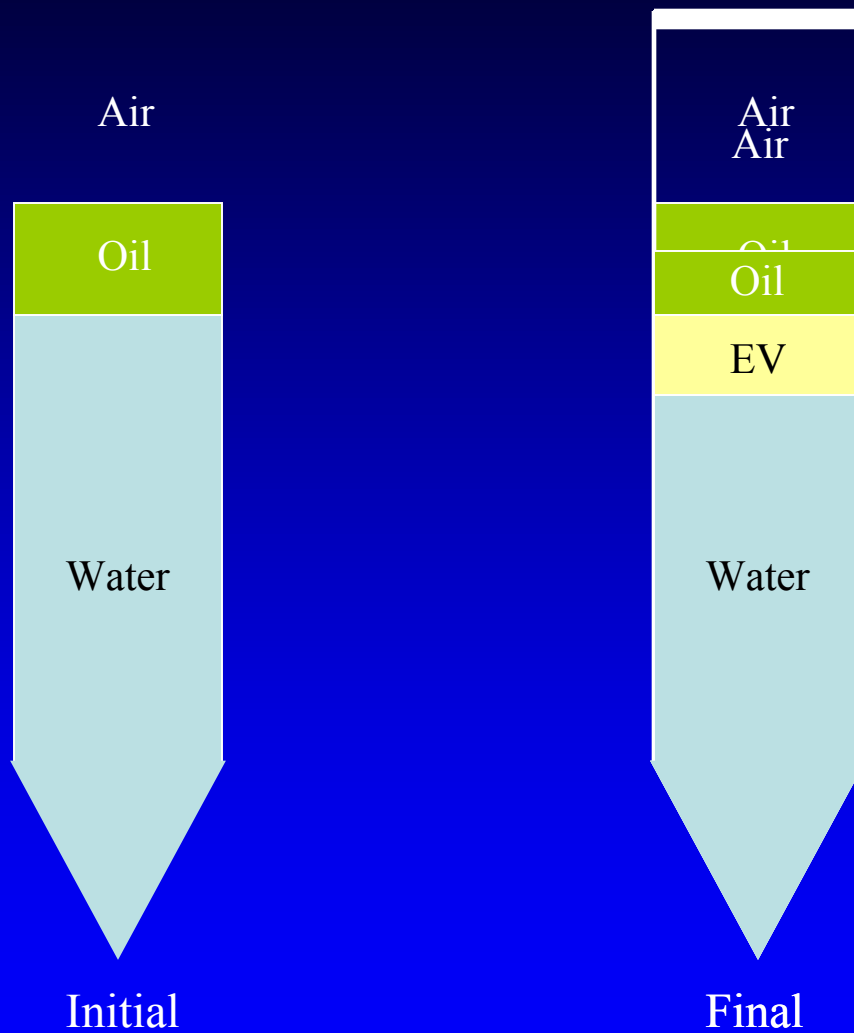
- Five vegetable oils
 - **Canola**, cottonseed, corn, soybean, peanut, sunflower
- Two petroleum oils
 - **South Louisiana Crude**, No. 2 Fuel Oil
- Water = 30 mL
- Oil = 1.00, **2.25**, 3.50, **4.75**, or 6.00 mL Oil
- Air = balance

Analyses



- Each sample was allowed to settle for one hour prior to analyses
- Dissolved organic carbon (DOC) in the water phase was measured
- Emulsification volume (EV) was recorded

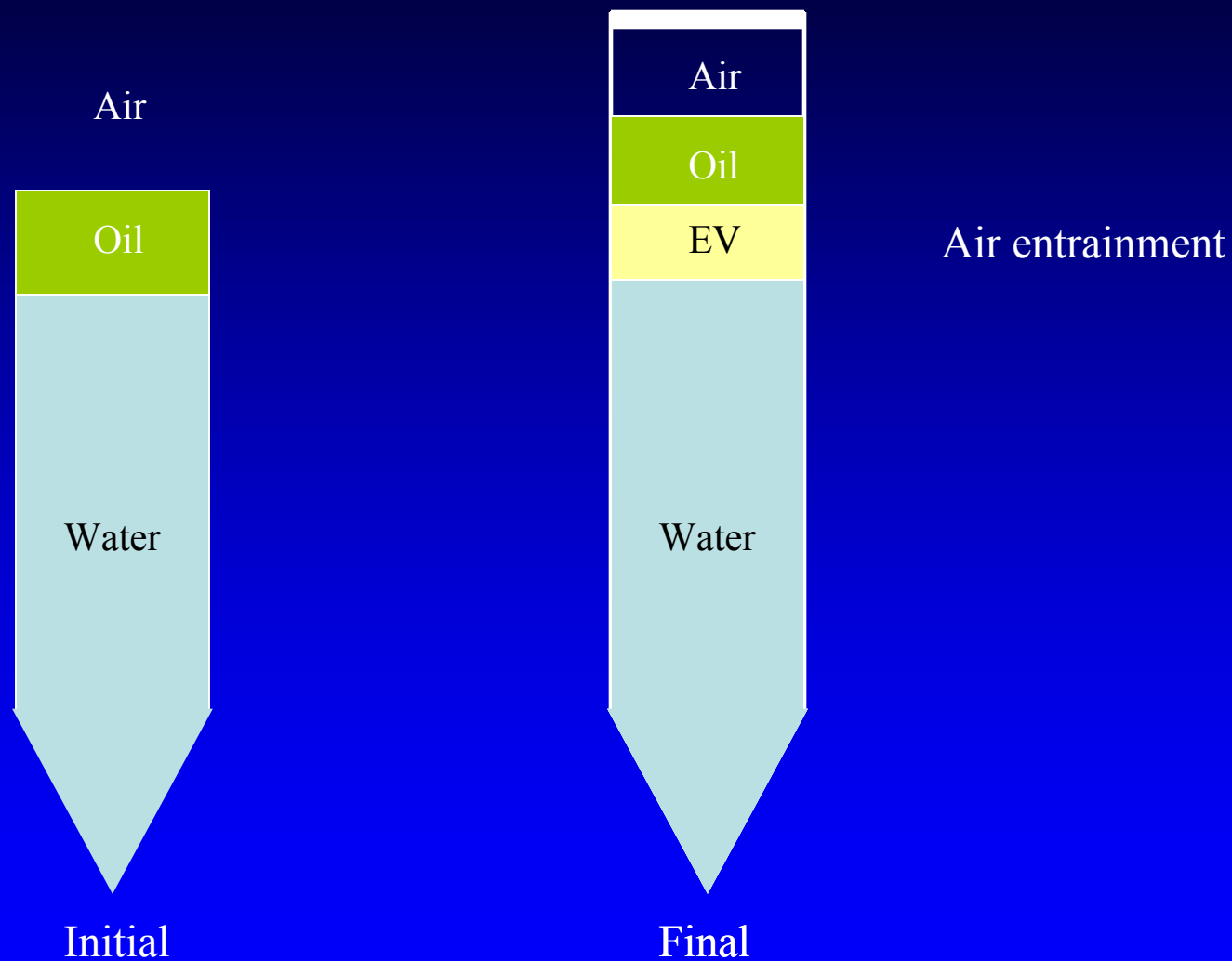
Possible Outcomes



Water-in-Oil (w/o) emulsion
Leak

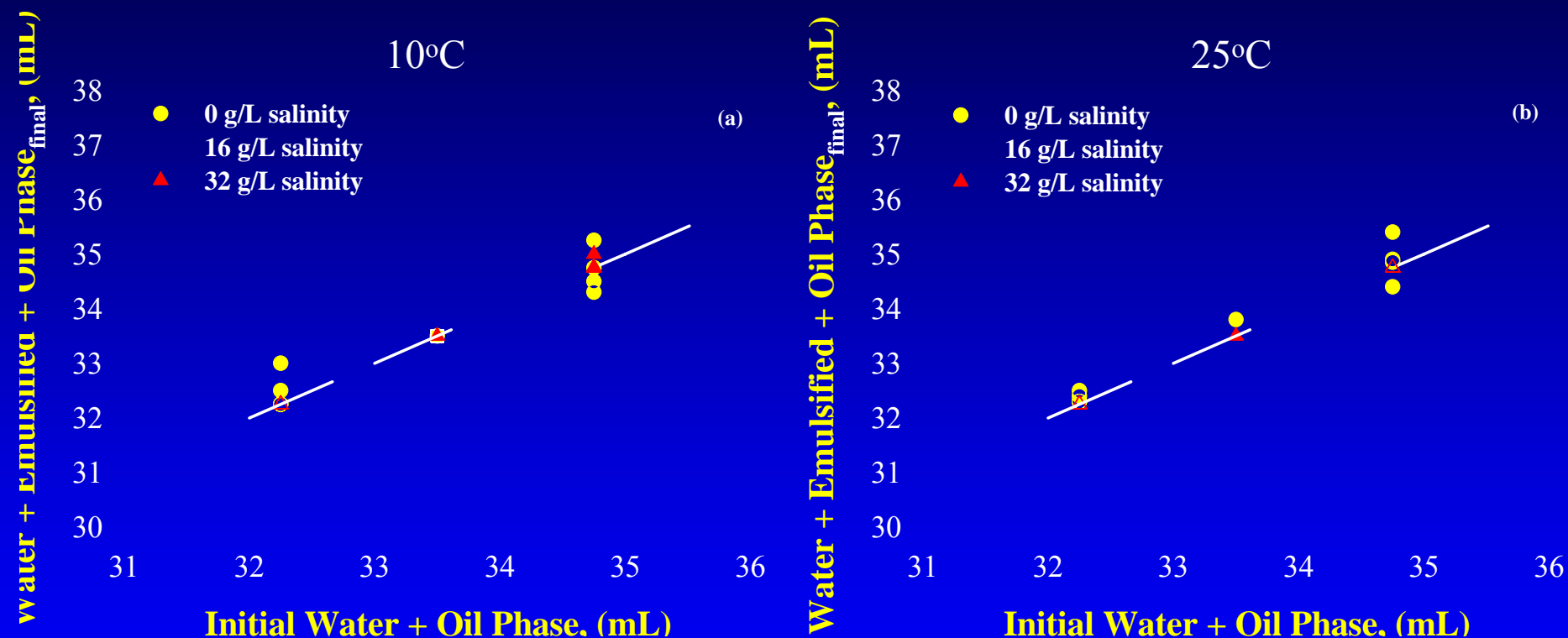
Oil-in-Water (o/w) emulsion

Possible Outcomes



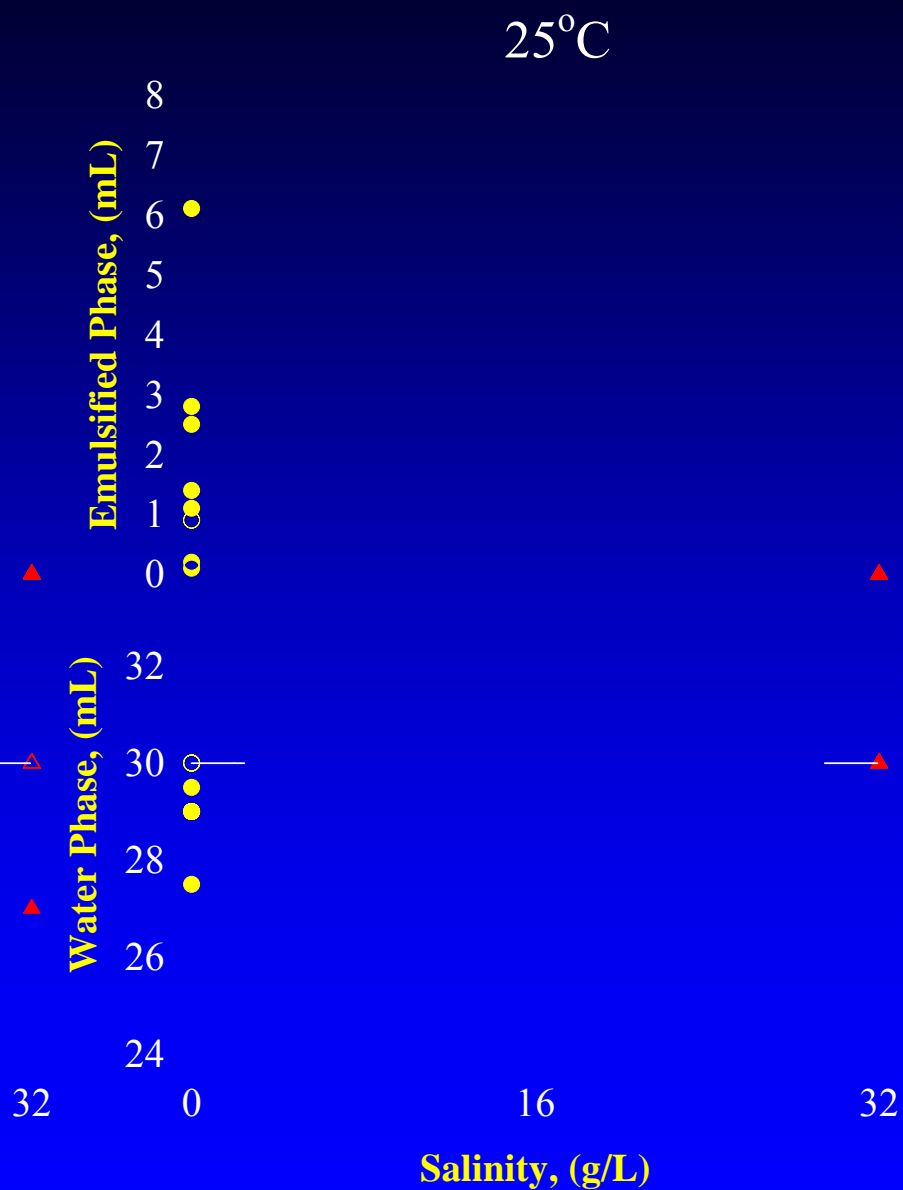
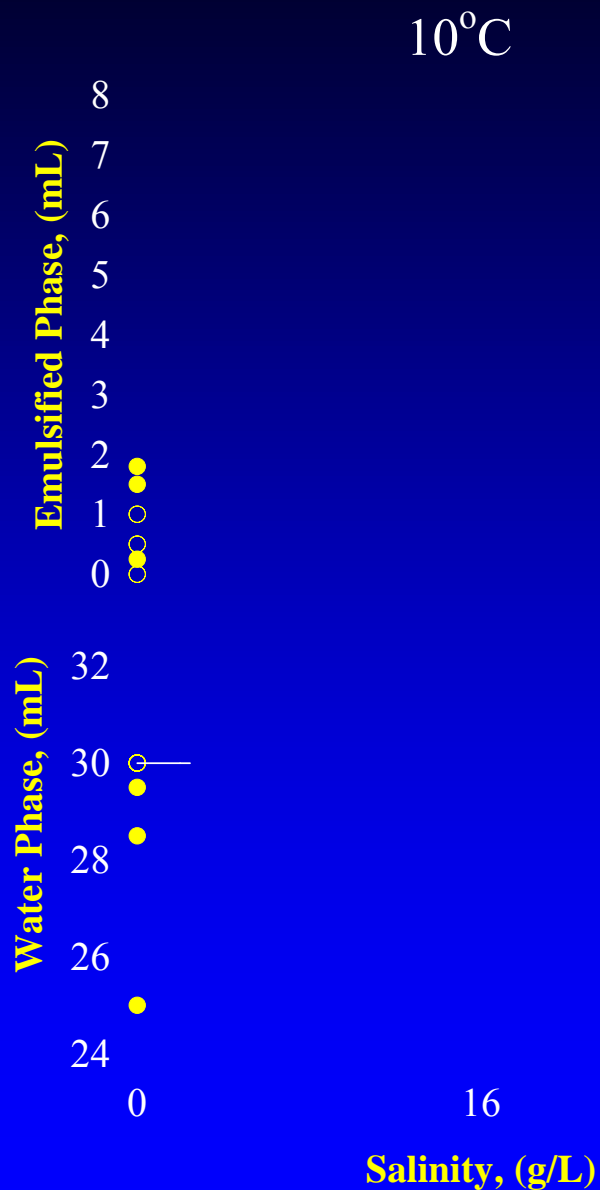
$$\Sigma (\text{Vol}_{\text{Oil}} + \text{Vol}_{\text{Water}})_{\text{Initial}} \leq \Sigma (\text{Vol}_{\text{Oil}} + \text{Vol}_{\text{Water}} + \text{Vol}_{\text{EV}})_{\text{Final}}$$

Canola oil

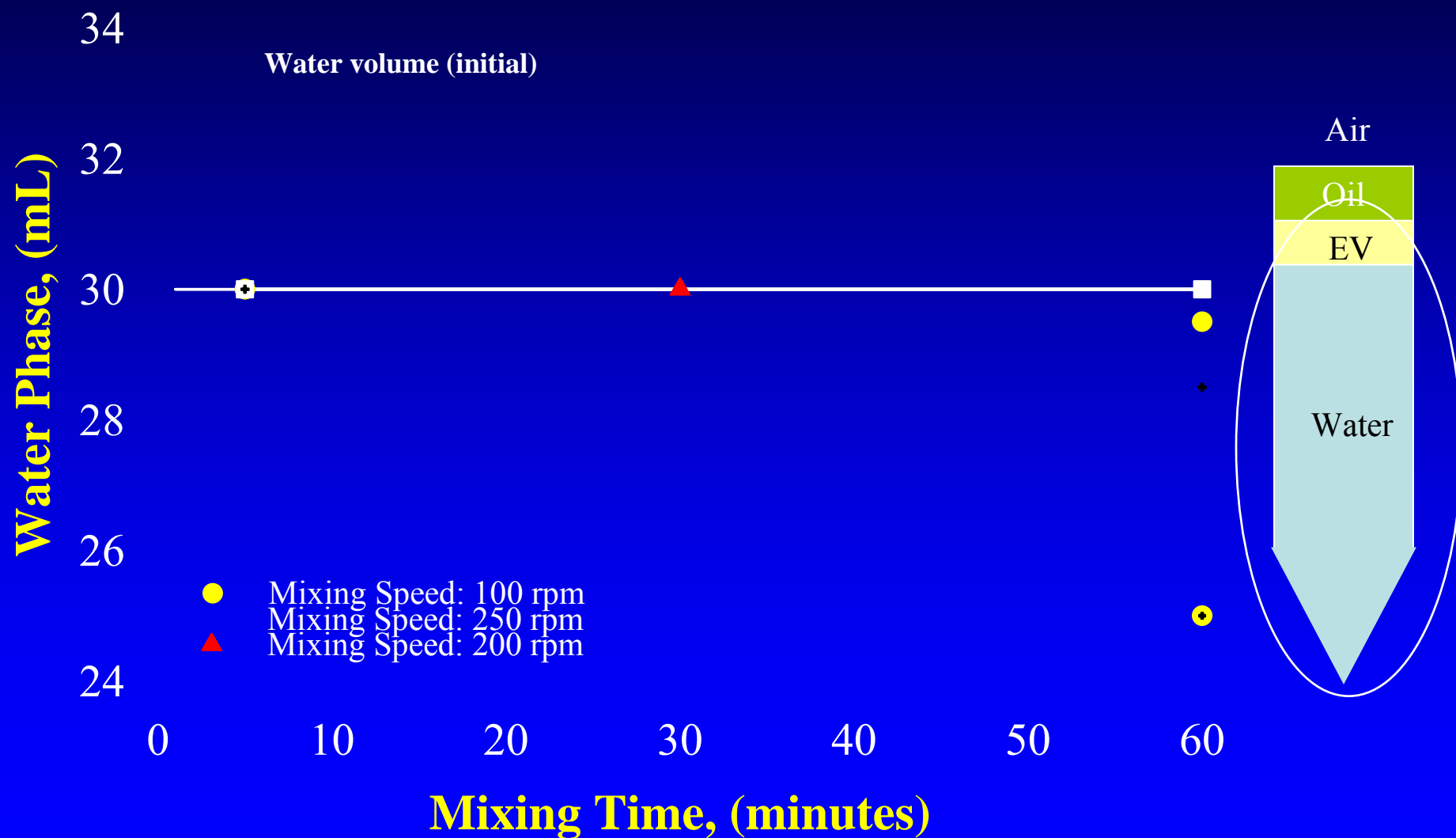


$$\Sigma (\text{Vol}_{\text{Oil}} + \text{Vol}_{\text{Water}})_{\text{Initial}} \leq \Sigma (\text{Vol}_{\text{Oil}} + \text{Vol}_{\text{Water}} + \text{Vol}_{\text{EV}})_{\text{Final}}$$

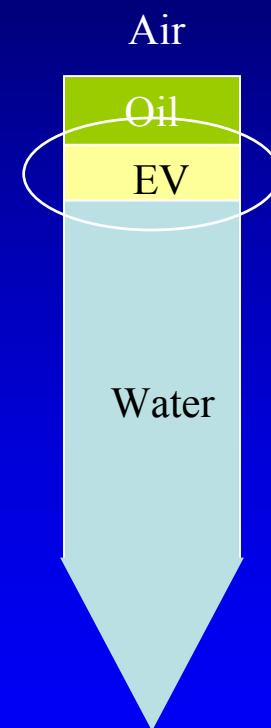
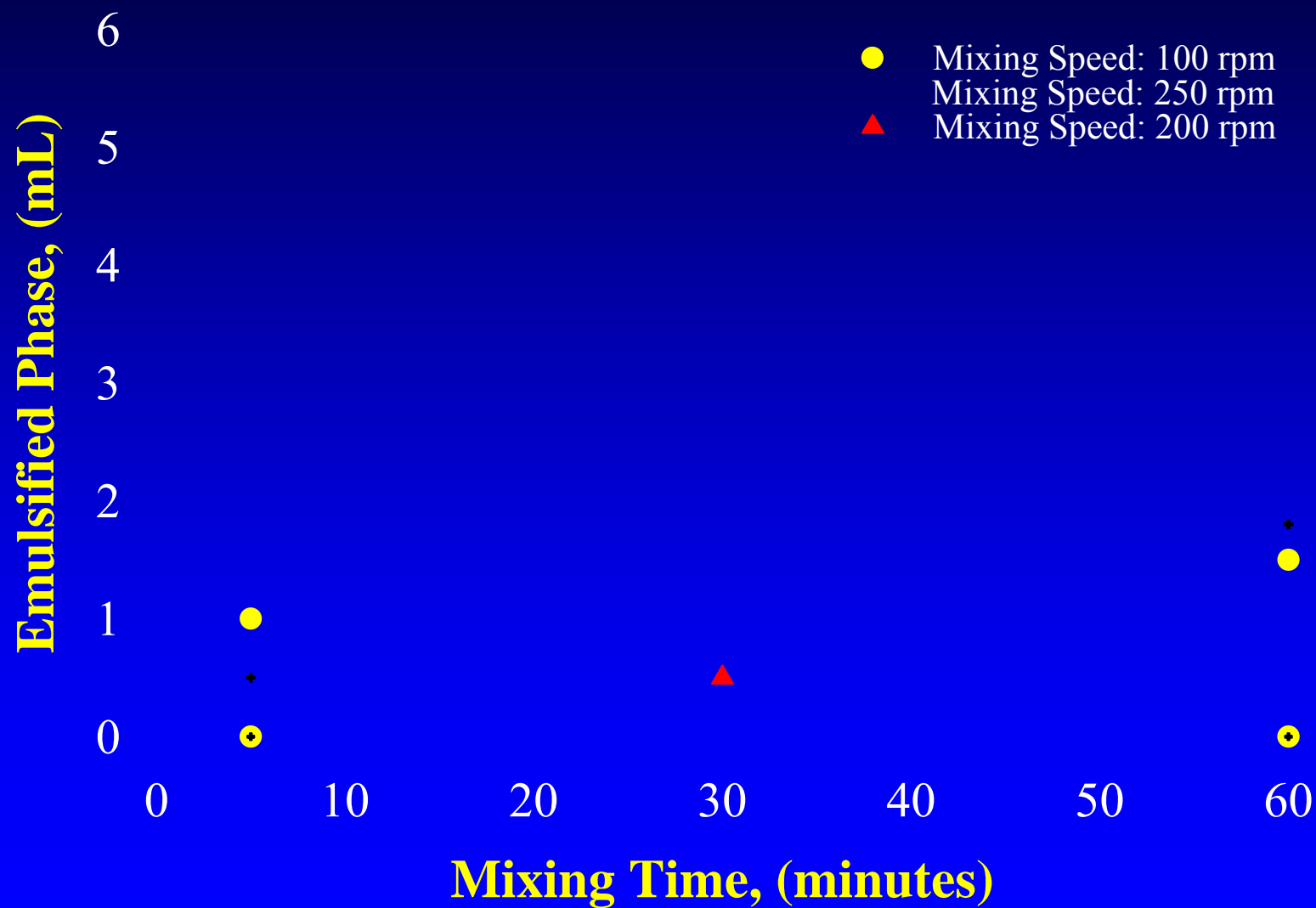
Effect of Salinity on Emulsification: Canola Oil



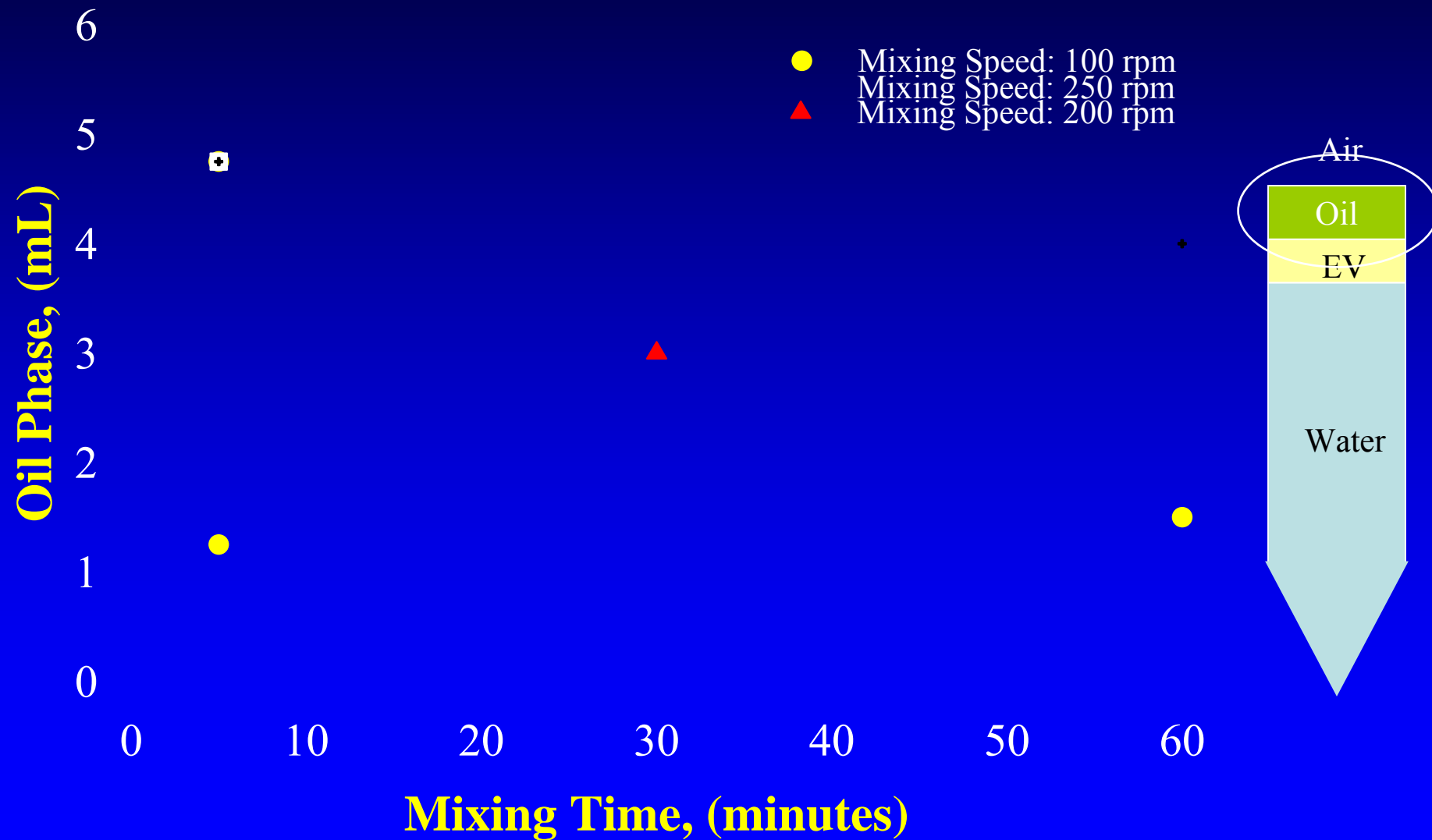
Canola Oil – 0 g/L NaCl; 10°C



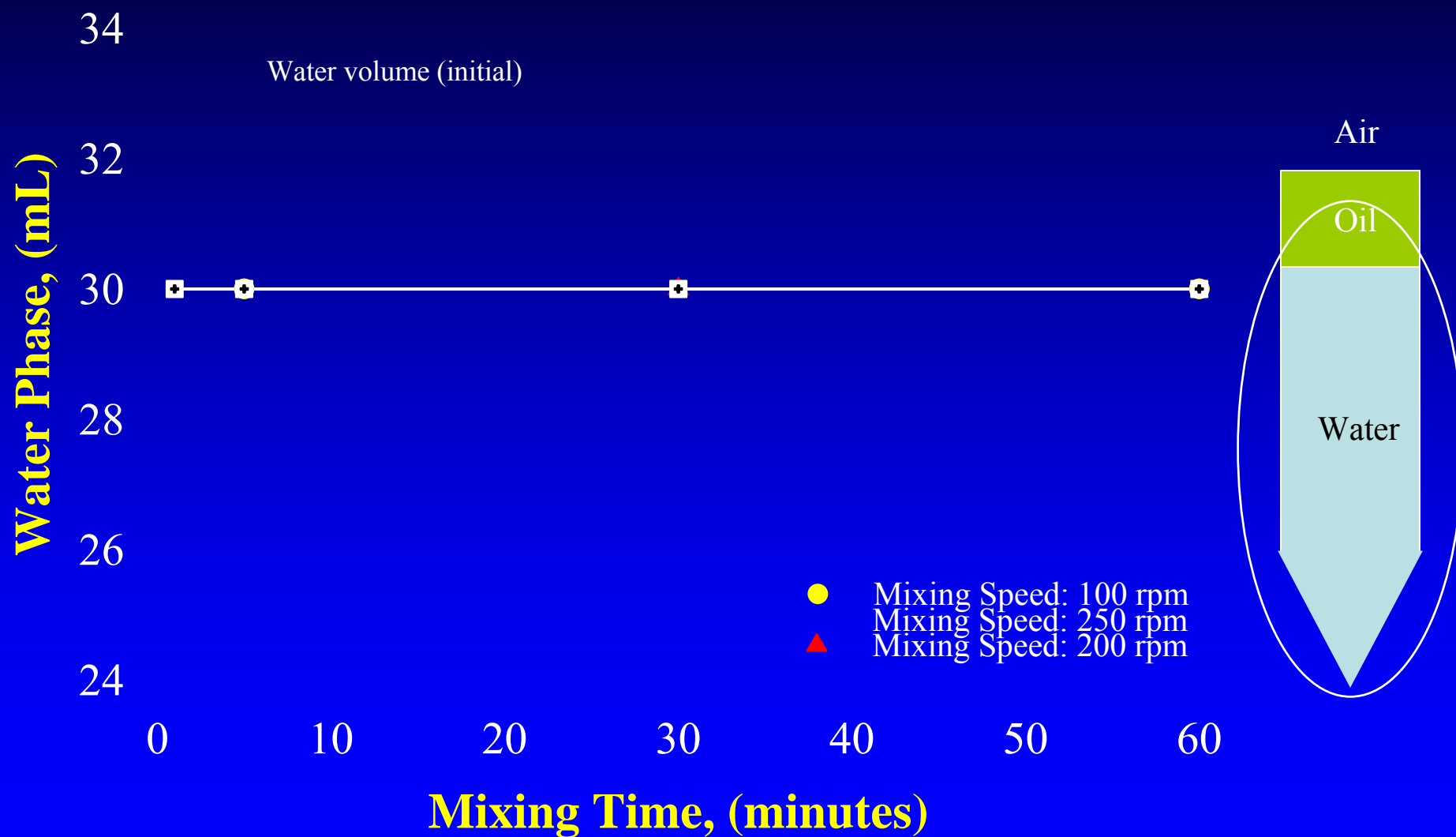
Canola Oil – 0 g/L NaCl; 10°C



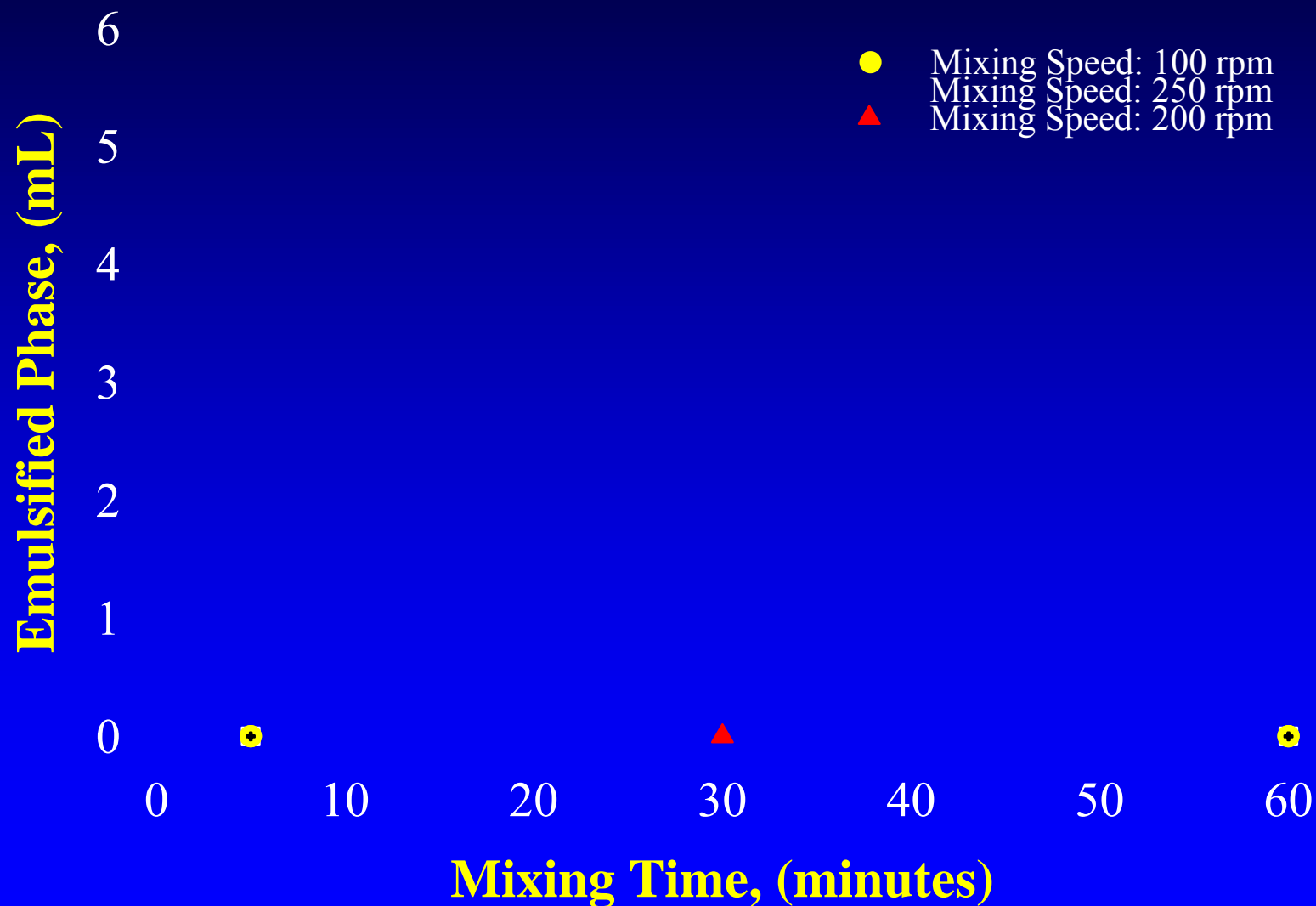
Canola Oil – 0 g/L NaCl; 10°C



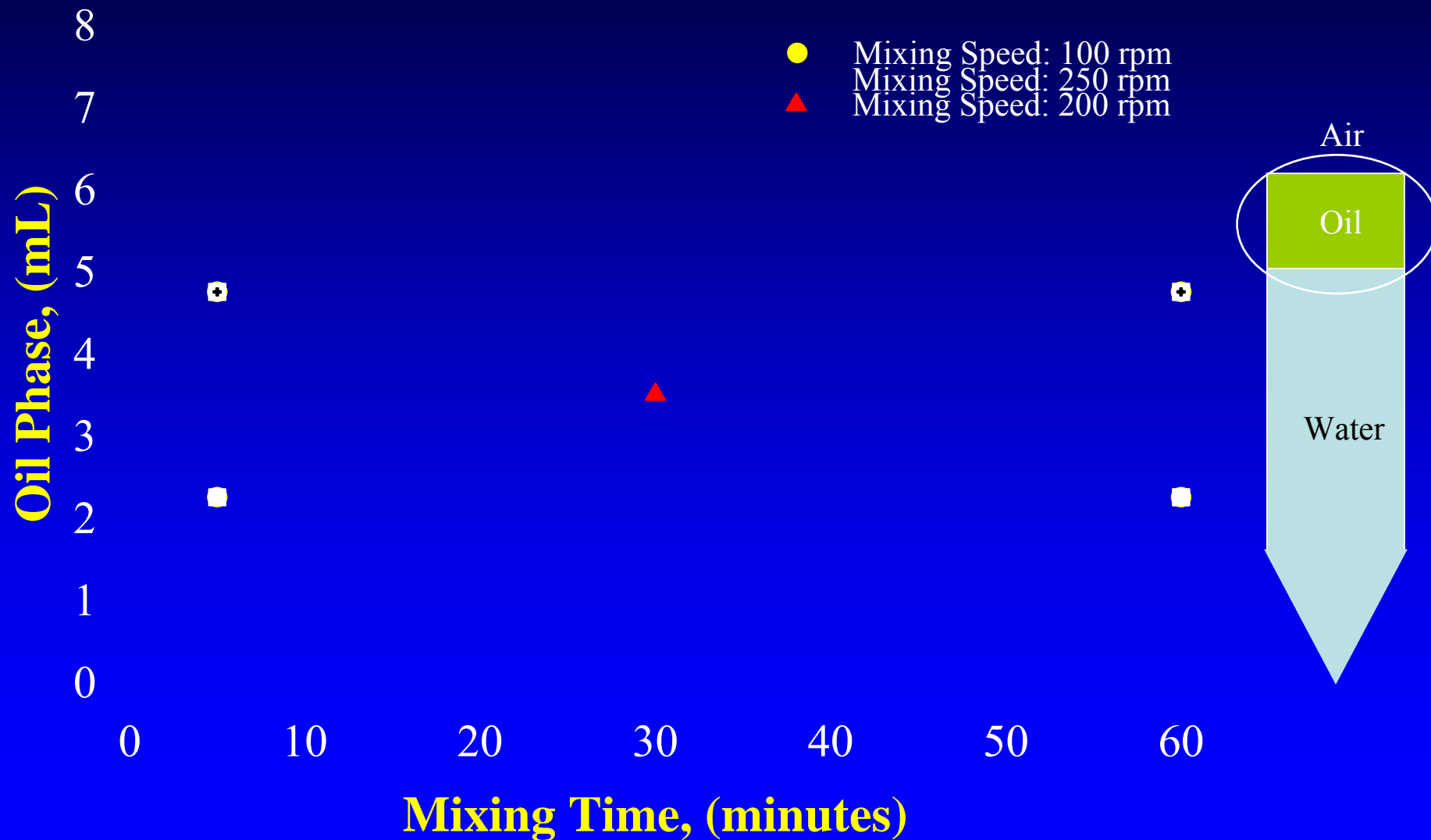
South Louisiana Crude Oil – 0 g/L NaCl; 10°C



South Louisiana Crude Oil – 0 g/L NaCl; 10°C



South Louisiana Crude Oil – 0 g/L NaCl; 10°C



Summary of results

- Data suggest a correlation between the volume of emulsified oil and the measured dissolved organic carbon
- Mixing time and salinity are important factors for emulsification
- Highest emulsification volumes were observed at the lowest salinity
- EV and DOC values for the petroleum oils were smaller than that for the vegetable oils

What is needed to determine Emulsification Factors

- Characterization of crude vegetable oils is needed
 - Identify emulsifying agents prior to experimental use
- Compare results from crude vegetable oil experiments with similar experiments using refined vegetable oils of similar triglyceride composition
- Consider longer mixing time
- Determine the effect of water hardness on emulsification
- Consider coconut and palm oils for high salinity experiments

Acknowledgment

- Original experimental data provided by Battelle